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A Luminescent $[Pd_4Ru_8]^{24+}$ Supramolecular Cage

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A phosphorescent cage of the form $[Pd_4Ru_8]^{24+}$ is reported. The cage was formed using the metalloligand $[Ru(dtbubpy)_2(qpy)]^{2+}$, where qpy = 4,4':2',2'':4'',4'''-quaterpyridine and dtbubpy = 4,4'-di*tert*-butyl-2,2'-bipyridine. The cage has been characterised by NMR, ESI-MS, TEM and X-ray diffraction analyses and its emission properties elucidated by steady-state and time-resolved emission spectroscopy.

Three dimensional metallosupramolecular self-assembly has evolved over the last thirty years as a powerful approach for the construction of structural frameworks, such as cages and capsules, with well-defined shapes and cavities.[1] Due to their ability to encapsulate guest compounds within their cavities, attention has now turned towards the use of these "supramolecules" as functional materials.[2] For instance, cages have been explored in the context of "artificial enzyme" catalysis,[3] for hazardous chemical capture,[4] reactive intermediate stabilisation,[2c] for drug delivery and release,[5] as well as in molecular sensing[6] and in biology.[7] More recently, desirable photophysical properties such as emission tuning,[8] encapsulation-assisted energy and electron transfer,[9] long-lived charge-separated state lifetimes[10] and photoresponsive guest uptake/release[11] have been achieved by integrating emissive moieties such as metalloporphyrins, metal complexes or fluorescent ligands, into the backbone of metallosupramolecular macrocycles and cages.[6a, 12]

Ruthenium(II) polypyridyl complexes can generally access multiple oxidation states, and they enjoy a rich history in photocatalysis.[13] However, Ru(II) complexes are general poorly emissive and their use as luminophores is limited.[14] Many examples have nevertheless been reported where ruthenium(II) complexes are incorporated into polymers,[15] networks,[16] metal-organic frameworks[17] and discrete 2D metallamacrocycles.[18] However, 3D supramolecular cages incorporating ruthenium(II) complexes as structural scaffolds still remain underexplored.[19] Three relevant examples of Ru(II) cages involve a Pd_8Ru_4 tetrameric cage[20] formed by the assembly of a Ru(II) metalloligand based on a 2,2',6',2"-terpyridine ligand and Pd^{2+} ions, a Pd_6Ru_8 cage,[21] in which the eight ruthenium metalloligands and the six Pd^{2+} ions are organised into an octahedron, and a L_4Ru_6 tetrahedral cage where L is 2,4,6-tri(pyridine-4-yl)1,3,5-triazine (tpt) and Ru is *cis*-bis(2,2'-bipyridine)ruthenium(II).[22] However, these cages as well as most of the supramolecular assemblies incorporating Ru(II) metalloligands are either poorly or non-emissive.

Herein we report, the structural characterisation of a cage of composition $[(\mathbf{Ruqpy})_8Pd_4]^{24+}$, **RuPd**, formed by self-assembly of the ruthenium(II) metalloligand $[Ru(dtbubpy)_2(qpy)][PF_6]_2$, **Ruqpy**, (where d*t*bubpy is 4,4'-di-*tert*-butyl-2,2'-bipyridine and qpy is 4,4':2',2'':4'',4'''-quaterpyridine) with Pd^{2+} ions. The **RuPd** cage has been characterised by NMR spectroscopy, ESI-MS spectrometry, TEM and X-ray crystallography. Notably, single crystal X-ray analysis revealed that **RuPd** has a diagonal distance of 38.4 Å (corresponding to the distance between furthest carbon atoms of opposite *t*-butyl groups), which makes it, to the best of our knowledge, the largest X-ray structure of a Ru(II) cage assembled with Pd^{2+} ions reported to date. The emission properties of **RuPd** have been investigated by steady-state and time-resolved photoluminescence spectroscopy and compared with those of the **Ruqpy** metalloligand.

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When two equivalents of **Ruqpy** were reacted with $[Pd(NCMe)_4](BF_4)_2$ in DMSO-d_6 at 85 °C for 12 h, the proton resonances associated with **Ruqpy** broadened and shifted downfield (Figure **1a**). The downfield shift of the signals of **RuPd** compared to **Ruqpy**, is evident for the pyridyl α- hydrogen atoms ($\Delta\delta$ = 0.23 ppm), and it is characteristic of metal-pyridine complexation. The broadness of the NMR signals of **RuPd** is indicative of the formation of a large structure, the motion of which is very slow on the NMR time scale (Figure **S1**). ^{1}H DOSY NMR spectroscopy clearly documents the formation of a single species in solution, the diffusion coefficient of which, measured in DMSO-d_6 was found to be D = 5.3 × 10^{-11} m^2/s. The magnitude of D correlates to the presence of a much larger structure than the metalloligand, which has a diffusion coefficient of 1.3 × 10^{-10} m^2/s in DMSO-d_6 (Figure **1b**). The calculated hydrodynamic radius (r_s) of the cage is 19.7 Å (Table **S1**). The presence of **RuPd** was further corroborated by HR-ESI-MS spectrometry, showing the isotopically resolved peaks for $[(\mathbf{RuPd})\text{-}(BF_4)_n]^{n+}$ (n = 7 - 9) that match with the simulated spectra (Figures **S6**-**S9**).

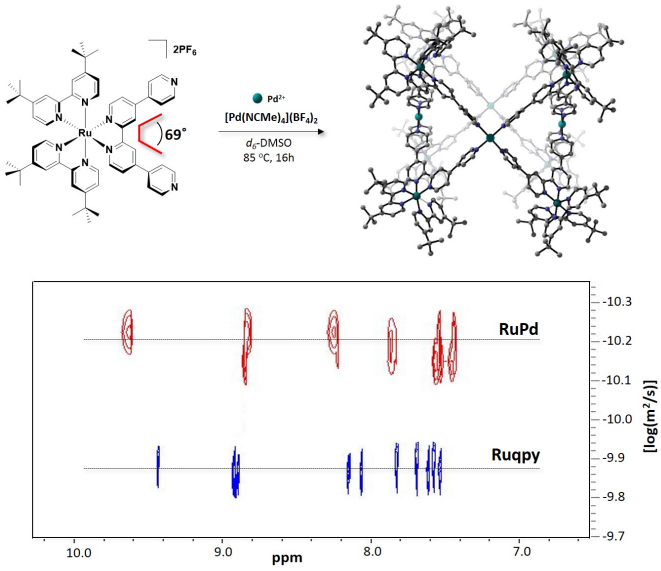

Figure 1. a) Self-assembly between **Ruqpy** and Pd^{2+} ions yielding the cage **RuPd,** showing the X-ray structure. **b)** ^{1}H DOSY NMR of **Ruqpy** in blue and **RuPd**, in red. The ^{1}H DOSY NMR spectra were collected in DMSO-d_6 at 298 K.

The cubic structure of **RuPd** was unambiguously determined by X-ray crystallography (Figures **1** and **2**). Crystals suitable for X-ray analysis were grown by the slow diffusion of a 1:1 mixture of ethyl acetate-hexane into a DMSO solution of **RuPd** (25 mM) over 40 days. The topology of **RuPd** resembles that reported by Klein *et al.* wherein the cage structure is constructed such that two ligands doubly bridge adjacent Pd(II) centres in a crown-like fashion, disposing the four palladium ions in a square arrangement.[23] This forms a metallomacrocyclic core to the cage. Among the family of Pd_4L_8 cages, this specific arrangement is rare with only six examples reported to date.[9c, 23-24] Indeed, this stoichiometry is only possible when the angle between the coordinating 4-pyridyl units is less than 90°; the X-ray structure of **Ruqpy** revealed that the angle between the coordinating 4-pyridyl units of the qpy ligand measures 69° (Figure **S3**). The angle between the coordinating 4-pyridyl units of **Ruqpy** is smaller than that of the previously reported complex $[Ir(mesppy)_2(qpy)]PF_6$, which showed a coordinating angle of 78°.[25] However, the assembly of both qpy-based complexes with Pd^{2+} ions gave rise to cages of the same Pd_4L_8 topology.[9c] The **RuPd** cage exhibits a longest diagonal of 38.4 Å (Figures **3**, **S3**), leading to a radius of the cage structure based on this diagonal of 19.2 Å, similar to that obtained by ^{1}H DOSY NMR analysis (r_s = 19.7 Å). The cage shows a distance between neighboring ruthenium atoms bridging the same Pd···Pd edge of 15.0 Å, an internal diameter of 27.4 Å (corresponding to the longest Ru···Ru distance), and a resulting internal volume of ca. 4900 $Å^3$. The nanostructures of cage **RuPd** were probed by Transmission Electron Microscopy (TEM) analysis upon deposition of **RuPd** (concentration of 1 x 10^{-6} M) onto carbon-coated copper grids (Figure **3**). The size of the nanostructures observed by TEM are of around 4.0 – 4.2 nm, in good agreement with the diagonal distance of 3.9 nm observed for the X-ray structure (Figure **3a**).

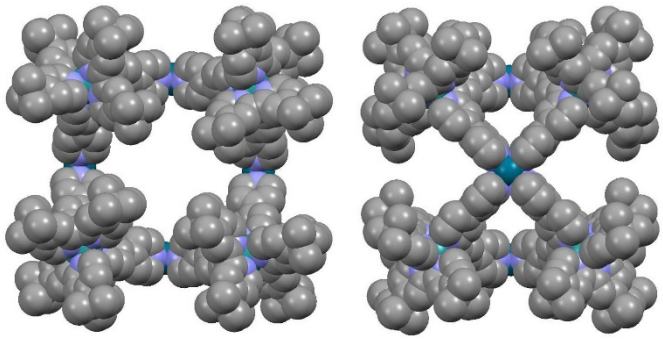

Figure 2. Space-filling views of the single crystal X-ray crystal structure of cage **RuPd** viewed down to the crystallographic *a*- (left) and *c*-axes (right). Hydrogen atoms, solvent molecules and counterions have been omitted for clarity.

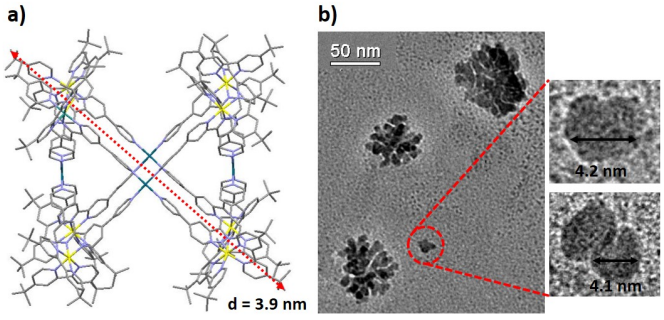

Figure 3. **a)** Illustration of the X-ray structure of **RuPd**, showing the diagonal distance across the long axis. **b)** TEM images of the nanostructures of **RuPd**.

The emission profile of **RuPd** in DCM (λ_{PL} = 710 nm) is broader and red-shifted compared to that of **Ruqpy** (λ_{PL} = 674 nm, Φ_{PL} = 7.3%), and with a photoluminescence quantum yield, Φ_{PL}, of 6.9% (Figure **4a**). Notably, the Φ_{PL} of **RuPd** is one of the highest reported among ruthenium cages. The red-shifted emission of **RuPd** compared to **Ruqpy** is the result of coordination of the Lewis acidic Pd(II) ions to the Ru complex, which essentially stabilizes the π^*_{qpy} orbital level involved in the emission, and thus lowers the energy of the triplet state.[26] Both **Ruqpy** and **RuPd** exhibit bi-exponential photoluminescence decay kinetics with lifetimes, τ_{PL}, of 324, 1047

ns and 151, 700 ns, respectively (Figure **4b**). As a result, similar radiative rate constants, k_r, of 6.97 x 10^4 s^{-1} and 9.86 x 10^4 s^{-1}, and non-radiative rate constants, k_{nr}, of 8.85 x 10^5 s^{-1} and 13.30 x 10^5 s^{-1} are obtained for **Ruqpy** and **RuPd**, respectively (Table **1**). Thus, the Pd(II) ions do not adversely affect the photophysical properties of this metalloligand. This observation is rather unusual considering that the emissions of the vast majority of metal complexes assembled within cage structures are often partially or fully quenched by the presence of Pd(II) ions,[19b, 20] likely due to the population of low-lying dark states involving the donor and acceptor units. The computational investigation (see details in the ESI) of **RuPd** reveals that the lowest possible transition, from the HOMO to the LUMO (see Figure **S12**), leads to a Rydberg excited state from d-based Ru orbitals to the Pd units. The presence of these parasitic states explains the slightly lower Φ_{PL} value (along with its increased k_{nr} value) for **RuPd** as compared to **Ruqpy**. The fact that, in this specific case, the photoluminescence is not completely quenched in the cage indicates that the radiative process is fast enough to compete with internal decay to the lowest-lying dark states.

Table 1. Photophysical properties of **Ruqpy** and **RuPd**.[a]

	λ_{PL} / nm	Φ_{PL} /%[b]	τ_{PL} / ns[c]	k_r x 10^4 / s^{-1}	k_{nr} x 10^5 / s^{-1}
Ruqpy	674	7.3	324 (0.2) 1047 (0.8)	6.97	8.85
RuPd	710	6.9	151 (0.1) 700 (0.9)	9.86	13.30

[a] Measurements in degassed DCM at 298 K (λ_{exc} = 360 nm). [b] Φ_{PL} measurements using quinine sulfate as the external reference (Φ_{PL} = 54.6% in 0.5 M H_2SO_4 at 298 K).[27] [c] λ_{exc} = 378 nm; values in parentheses are pre-exponential weighting factor, in relative % intensity, of the emission decay kinetics.

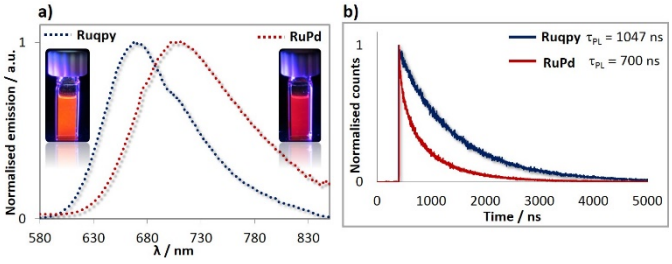

Figure 4. **a)** Normalised emission spectra of **Ruqpy** (dotted blue line) and **RuPd** (dotted red line) in degassed DCM at 298 K (λ_{exc} = 360 nm). Photographs of the emissions of **Ruqpy** (left) and **RuPd** (right) are inset to the spectra. **b)** Emission decays of **Ruqpy** (blue line) and **RuPd** (red line) in degassed DCM at 298 K (λ_{exc} = 378 nm).

In conclusion a NIR luminescent cage of composition $[Ru_8Pd_4]^{24+}$, formed through the self-assembly of the ruthenium metalloligand $[Ru(dtbubpy)_2(qpy)][PF_6]_2$ with Pd^{2+} ions has been reported. The structure of the ruthenium cage has been elucidated by X-ray diffraction and its emission properties investigated by steady-state and time-resolved emission spectroscopy. Cages and capsules based on ruthenium(II) complexes are very rare and are generally poorly- or non-emissive. However, **RuPd** exhibits a photoluminescence quantum yield of 6.9%, which is remarkably high, considering the emission maximum of 710 nm. The use of the red-emitting cage **RuPd** as a photosensitiser to induce photochemical transformations of bound guests in water is currently under investigation in our laboratory, the results of which will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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